Standard Addition Calculation and Error Analysis.

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You are interested in determining the concentration of an unknown solution C by fluorescence using the method of standard addition. Let's assume that you've made five solutions C + nΔ where n= 0-4, and measure five fluorescence values, F0 – F4. This leads to five (x,y) data points:

(C, F0), (C + Δ, F1), (C + 2Δ, F2), (C + 3Δ, F3), (C + 4Δ, F4).

If we graph the following five (x,y) data points:

(0, F0), (Δ, F1), (2Δ, F2), (3Δ, F3), (4Δ, F4).

We will get a straight line that can be fit with the linear equation

$y = mx + b$

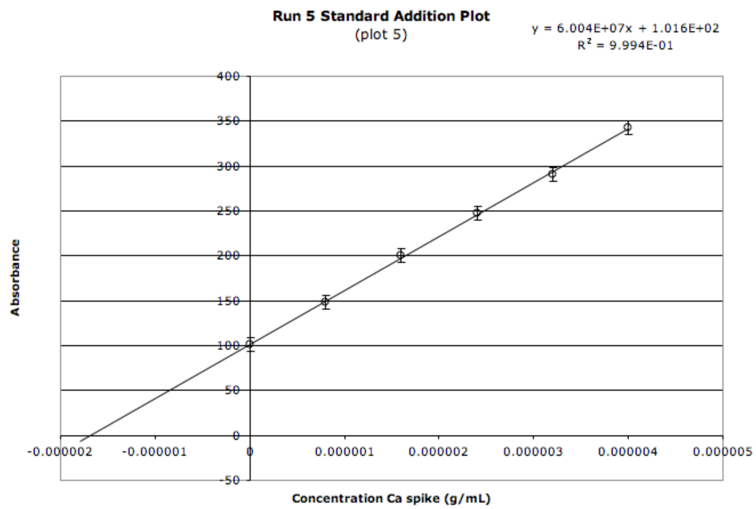
This line is the same line as a standard calibration curve, but shifted to the left by an amount equal to –C. To get the value of C, we set y=0 and calculate the value for the x intercept x_0 = x at y=0:

$x_0 = -b/m = -C$

therefore:

$C = b/m$ in units of Δ.

Here's a picture from Wikipedia:



Error analysis for the method of standard addition:

$C = b/m$

95% C.L. = $\pm\, t_{N-2}\, s_c$

We need to calculate s_c. Here's the result of the statistical derivation:

$$s_c = \frac{s_r}{m}\sqrt{\frac{1}{N} + \frac{(\bar{y})^2}{m^2 S_{xx}}}$$

This equation is similar to the equation we use for the linear calibration curve from Skoog with $y_c = 0$ and no 1/C term.